

THERMAL CRACKING OF NATURAL BITUMEN IN PRESENCE OF ACTIVATING ADDITIVES

Yerdos K. Ongarbayev^{1,2}, Yerzhan Imanbayev^{2,4}, Yerbol Tileuberdi^{1,2}, Shynar A. Oteuli¹,
Ainur B. Zhambolova¹, Zulkhair A. Mansurov^{1,2}, Evgenii B. Krivtsov³, Anatolii K. Golovko³

¹ Al-Farabi Kazakh National University,
71, Al-Farabi str., 050040, Almaty, Kazakhstan

² Institute of Combustion Problems,
Bogenbay batyr str., 172, 050012 Almaty, Kazakhstan

³ Institute of Petroleum Chemistry, Siberian Branch, Russian Academy of Sciences
634055, Akademicheskii pr., 4, Tomsk, Russia

⁴ Yessenov University, 130003, 32 microdistrict, Aktau, Kazakhstan
E-mail: Erdos.Ongarbaev@kaznu.kz

Received 22 February 2018
Accepted 05 December 2018

ABSTRACT

The paper presents the results of thermal cracking of natural bitumens of the Beke and Munaily Mola oil sand deposits (Kazakhstan). The data obtained show that the high-molecular components of the bitumen of the Munaily Mola deposit are more easily cracked than those of the Beke deposit. The cracking of natural Beke bitumen in a medium of water vapor, acetonitrile and isopropanol is studied at different temperatures and pressures. The effect of the heterogeneous additive – nano-sized copper (II) oxide on the cracking efficiency of natural bitumen components is identified. The total yield of gas and coke is 3.2 %, while the distillate fractions is 40.8 mass % in case of cracking of the Beke natural bitumen in a flow reactor.

Keywords: oil sand, natural bitumen, cracking, NMR analysis, molecular mass.

INTRODUCTION

The heavy oils and natural bitumen are an important source of raw materials required because of the growing demand for fuel as the stocks of light and medium oils decrease. The world resources of heavy oils and natural bitumen exceed significantly the reserves of light oils and are estimated at more than 810 billion tons. The involvement of the natural bitumen in refining requires the modernization of the existing schemes and the development of new, more efficient technologies for processing them aiming maximum possible number of light fractions and their quality increase.

The heavy oils and natural bitumen are characterized by a high content of aromatic hydrocarbons, tar-asphaltene substances, a high concentration of metals and sulfur compounds, an increased coking ability. The development of effective methods of processing

and further use of heavy oil conversion products or natural bitumen requires knowledge of the effect of the temperature and nature of the catalysts in view of the various functional groups in the structure of the resins and asphaltene molecules. This data is important for a deeper understanding of the changes that occur in the latter in the course of the processes of thermal and catalytic cracking, the selection of optimal schemes for the installations modernization and the determination of the processing modes of heavy hydrocarbon feedstocks by the refineries [1 - 3].

The thermal catalytic conversion of a heavy hydrocarbon feedstock in a solvent medium (under critical or supercritical conditions) in the presence of catalytic additives, for example, various oxides [3 - 7] is a promising method for producing synthetic crude oil. The peculiarities of this process refer to the interaction of the solvent vapors with the catalysts with the formation

of hydrogen participating in the hydrogenation reactions (preventing recombination of the formed radicals) and hydrocracking. They proceed along with the processes of oil components destruction. For example, water under supercritical conditions has the properties of a non-polar proton-donor solvent [8-13] thus providing significant increase of the efficiency of the thermal processes of destruction of heavy oil feedstocks. "Synthetic" oil of a low content of high molecular weight and heteroatomic compounds and high content of low-boiling fractions is obtained.

The aim of this investigation is to develop a method for thermocatalytic destruction of the components of the natural bitumen from the oil sands of the Republic of Kazakhstan. The influence of the solvents (water, acetonitrile, isopropanol), a heterogeneous catalyst additive (nano-sized copper (II) oxide) and the heat treatment conditions (a stationary or a flow reactor) on the composition of the cracking products of the natural bitumen of the Beke deposit is studied.

The choice of the nano-sized copper oxide is determined by the fact that copper is a transition metal with an unfilled shell of the first subgroup. Besides, it has a catalytic activity in relation to many hydrogenation, dehydrogenation and hydrogenolysis reactions of the heavy oil heteroorganic compounds [14].

EXPERIMENTAL

The oil sands of the Beke and Munaily Mola deposits (Kazakhstan) were the object of the study.

The bitumen cracking was carried out in an autoclave of a volume of 12 cm³. The bitumen weight was 7 g. According to the previous studies results [15], the temperature of the bitumen heat treatment was 450°C, while the duration was 60 min. A heat treatment time of less than 60 min did not provide a high extent of transformation of the high molecular mass components. The increase of the heat treatment time resulted in significant increase of the yield of the solid products (coke). The mass of the reactor in absence of a sample was fixed. After the thermal treatment of the bitumen, the yield of the gaseous products was determined on the ground of the loss of the mass of the reactor with a sample after gas products removal. The selected gaseous products were analyzed using a gas chromatograph. After sampling the liquid products, the reactor was washed with

chloroform and weighed. The difference between the reactor mass prior to the experiment and after it was determined as a coke.

The installation for bitumen thermal cracking provided carrying out experiments under the following conditions: variation of the maximum pressure until reaching a value of 100 atm, a reactor operating temperature increase until reaching a value of 600°C. This installation provided automatic maintenance of the process temperature, raw materials supply at a given rate, sampling of the gaseous and liquid products.

Due to the small amount of liquid product produced in the course of the experiments, the analysis of the fractional composition of the liquid products by the standard method [16] was impossible. Therefore, the light fractions content in these products was estimated on the ground of a thermogravimetric analysis. The latter was carried out in air using a derivatograph of MOM (Hungary). It provided the recording of the loss of the sample mass in case of temperature increase to 350°C with a heating rate of 10 deg/min.

The group composition of the initial bitumen and the liquid cracking products was established according to the traditional scheme: first, the content of asphaltenes in the sample was determined by the "cold" method of Golde. The concentration of the resins in the resulting maltenes was determined by the adsorption method. It required the application of the analyzed product to activated silicagel, the placement of the mixture in the Soxhlet extractor and sequentially flushing of the hydrocarbon components (oils) with n-hexane, while that of the resin - with an ethanol-benzene mixture of a ratio of 1:1.

RESULTS AND DISCUSSION

The results referring to the physical and chemical characteristics and composition of the initial natural bitumen are presented in Table 1. The objects are characterized by high density and high molecular weight components – resins and asphaltenes (more than 50 mass %). The bitumen of the Beke deposit has a density of more than 1100 kg/m³, while that of Munaily Mola – more than 990 kg/m³. The total heteroatoms content in the bitumens does not exceed 5 mass %. The differences in their quantity are insignificant - only the content of oxygen in the bitumen of Munaily Mola is noticeably greater than that of the bitumen of Beke. The

Table 1. Physical and chemical characteristics of the initial bitumens.

Parameters	Deposit of bitumens	
	Beke	Munaily Mola
Density, kg/m ³	1112.2	992.1
Coking ability, %	30.1	35.0
Element composition, mass %:		
C	84.8	84.7
H	11.7	11.4
N	0.6	0.4
S	1.5	1.4
O	1.5	2.1
H/C ratio	1.6	1.6
Fractional composition, mass %:		
Boiling point. °C	116.8	96.5
BP – 200 °C	5.1	2.2
200 – 360 °C	20.2	15.6

H to C ratio for both bitumens is slightly greater than 1.6, which indicates a high content of hydrogen and aromatic structures content of the bitumen components. The bitumens differ in their fractional composition: the boiling point (BP) is 96.5°C and 116.8°C, the yield of the gasoline fractions (BP-200°C) is 5.1% and 2.2 %, and of the diesel fractions (200°C - 360°C) – 20.2 % and 15.6 mass %, respectively.

The material balance of the products of bitumen thermal cracking is presented in Table 2. A significant amount of coke (more than 30 %) is obtained in case of thermal cracking of the Beke deposit bitumen. The degree of its resin breakdown is 57.4 % rel., while the oils yield in the liquid products is 41.5 %. This is 7.8 % less than that of the initial bitumen. The increase of the asphaltenes amount of the Beke deposit is related to

the high content of heavy uncracking resin compounds. They form stable asphaltene of a higher molecular mass.

The thermal cracking of the bitumen of Munaily Mola deposit results in 26.2 % of solid products (coke), which is 4.7 % less than that of bitumen of the Beke deposit, and 7 times less than that of the gaseous products. As in the case of the bitumen of the Beke deposit, the resin of the bitumen of Munaily Mola deposit is also easily destroyed and the degree of its destruction reaches a value of 78.9 % rel. Unlike the Beke deposit bitumen, the content of oils in the liquid products of the cracked bitumen of the Munaily Mola deposit increases to 14 %. The asphaltenes content of the liquid cracking products of the Munaily Mola bitumen is decreased by 3.8 % in comparison with their content in the initial bitumen.

The data obtained shows that the high-molecular

Table 2. Material balance and bulk composition of thermal cracking products of bitumens in stationary state.

Sample of bitumen	Content, mass %					
	Gas	Coke	Liquid products			
			Total	Oils	Resins	Asphaltenes
Initial bitumen of Beke deposit	0	0	100.0	49.2	44.8	5.9
After cracking of bitumen of Beke deposit	1.4	30.9	67.7	41.5	19.1	7.1
Initial bitumen of Munaily Mola deposit	0	0	100.0	47.6	46.4	6.0
After cracking of bitumen of Munaily Mola deposit	0.2	26.2	73.6	61.6	9.8	2.2

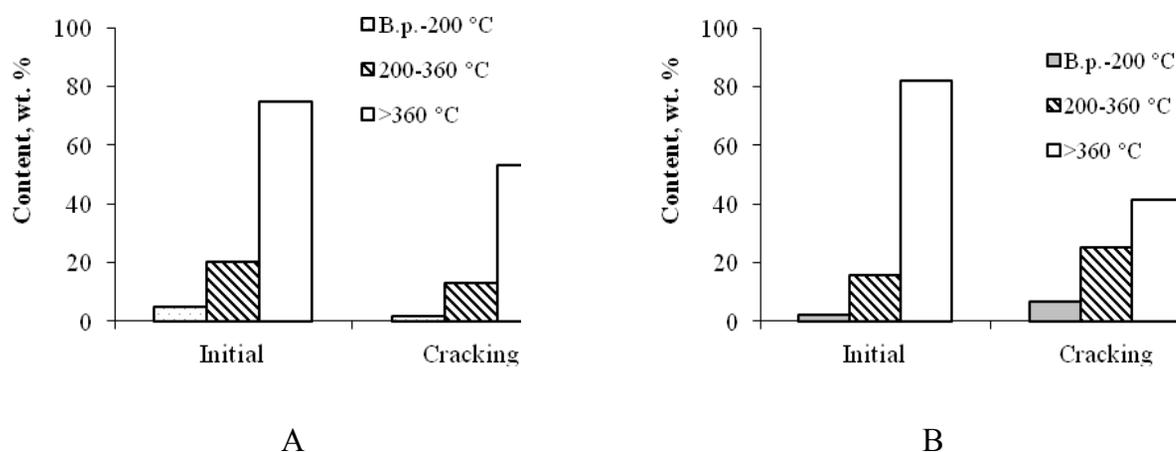


Fig. 1. Fractional composition of natural bitumen and liquid cracking products.
Bitumens: A - Beke deposit, B - Munaily Mola

components of the bitumen of the Munaily Mola deposit are more easily cracked than those of the Beke deposit.

The analysis of the fractional composition of the bitumen cracking products (Fig. 1) shows that when the bitumen of the Beke bitumen is cracked, the content of both gasoline and diesel fractions decreases by 3.5 mass % and 7.4 mass %, respectively. In the case of Munaily Mola bitumen, on the contrary, there is an increase of

gasoline (by 4.6 %) and diesel (by 9.6 mass %) fractions.

Table 3 shows the distribution of protons in the structural fragments of the averaged resin molecules and asphaltenes of the initial bitumens and liquid cracking products (data obtained from ^1H NMR spectroscopy). During the cracking process, the bitumen resins undergo changes due to their destruction. Formation of resinous structures differing in their parameters from those of

Table 3. ^1H NMR spectra and molecular weights of resins and asphaltenes of the initial bitumens and their cracking products under stationary state conditions.

Sample of bitumens	Molecular weight, Da	Content, %			
		H_{ar}	H_{α}	H_{β}	H_{γ}
Resins					
Initial bitumen of Beke deposit	751	4.82	14.40	67.21	13.56
After cracking of bitumen of Beke deposit	499	7.45	14.88	63.29	14.38
Initial bitumen of Munaily Mola deposit	556	6.03	15.32	56.83	21.82
After cracking of bitumen of Munaily Mola deposit	437	15.89	26.79	44.40	12.92
Asphaltenes					
Initial bitumen of Beke deposit	2044	14.28	24.97	45.94	14.81
After cracking of bitumen of Beke deposit	1304	14.75	24.63	50.19	10.43
Initial bitumen of Munaily Mola deposit	1803	19.67	33.66	38.74	7.93
After cracking of bitumen of Munaily Mola deposit	677	23.96	28.87	36.42	10.76

Table 4. Composition of thermal cracking products of Beke bitumen in stationary conditions.

Composition products	Initial bitumen	Composition of cracking products, mass %		
		Additions		
		*1	*2	*3
Liquid products, including:	100.00	72.7	67.5	75.0
- Oils	49.2	43.6	43.3	58.9
- Resin	44.9	3.9	7.3	8.8
- Asphaltene	5.9	25.2	16.9	7.3
Solid	–	23.8	27.3	19.3
Gaseous	–	3.4	8.5	5.7
1 - H ₂ O + acetonitrile; Bitumen/acetonitrile/water ratio = 4/3/1;				
2 - H ₂ O + acetonitrile + CuO (1 wt.%), Bitumen/acetonitrile/water ratio = 4/3/1;				
3 - Isopropyl alcohol + CuO (1 wt. %), isopropyl alcohol/bitumen ratio = 2/3.				

the initial one proceeds. Thus, the molecular weight of the resin molecules of the cracking products of the Beke bitumen decreases 1.5 times, while the fraction of aromatic fragments in the averaged molecule increases 1.5 times – the proportion of the protons in the aromatic structures of H_{ar} increases from 4.82 % to 7.45 %, while the proportion of the protons of the terminal groups (H_γ) increases from 13.56 % to 14.38 %. The proportion of the protons of the groups in α-position to the aromatic nucleus remains almost unchanged. The share of H_β protons decreases, which indicates a slight destruction of the aliphatic fragments of the resin molecules during the cracking process. These data indicates the preferential course of the aromatization reactions of the naphthenic cycles in the Beke bitumen resin molecules under thermal cracking conditions.

The molecular mass of the resins decreases insignificantly (from 556 to 437) in the course of cracking of the bitumen of the Munaily Mola. This is in comparison with the data referring to the bitumen of the Beke deposit. The number of the aromatic protons H_{ar} increases more than 2 times. The protons in H_α aliphatic fragments increase also. The share of protons of the terminal groups (H_γ) and the size of H_α aliphatic substituents (H_β) decrease substantially. These data indicates a deeper degradation of the bitumen resins from the Munaily Mola deposit compared to bitumen from the Beke deposit.

The protons of the terminal groups (H_γ) of asphaltenes of the bitumen of the Beke deposit cracking products decrease by 4.38 %, while H_β increases by 4.25

%. Most likely, this is explained by the cyclization of the aliphatic fragments with the formation of naphthenic cycles. The asphaltenes molecular mass decreases by 740 Dalton.

For asphaltenes of the Munaily Mola deposit bitumen, the fraction of H_α and H_β falls by 4.79 % and 2.32 %, while the molecular mass decreases by 1126 Da. The values of H_{ar} and H_γ increase by 3.99 % rel. and 2.83 % rel.

It is found that the cracking of the bitumen from the Beke deposit leads to a deterioration of the fractional and material composition of the liquid cracking products due to cyclization and aromatization reactions. The cracking proceeds along the pathway: a resin → asphaltenes → a coke.

Therefore the next stage of the research is focused on the determination of the effect of various additives (water, isopropyl alcohol, acetonitrile, copper oxide) on the composition of the Beke bitumen cracking products in an autoclave reactor under stationary conditions for duration of 1 h at a temperature of 450°C. The results obtained are presented in Table 4. The introduction of additives to the cracking process leads to an increase of the yield of the gaseous products (until 3.4 % - 8.5 %), that of oils (until 43.3% - 58.9 %) and the asphaltenes (until 7.3 % - 25,2 %), while the resins proportion is significantly decreased (to 3.9 % - 8.8 %).

The greatest yield of the target products is achieved by introduction of isopropanol (isopropyl alcohol/bitumen ratio = 2/3) and 1 mass % of copper oxide. The

Table 5. Bulk composition of bitumen cracking products in different conditions.

Process	S _{total} in oils, wt. %	Composition of liquid products, mass %		
		Oils	Resins	Asphaltenes
Initial bitumen	0.3	49.2	44.9	5.9
Cracking in autoclave	0.4	41.5	19.1	7.1
Bitumen + isopropanol + CuO in flow conditions	0.3	56.6	24.3	15.3

total yield of the liquid products is 75.0 %, that of oils amounts to 58.9 %, that of resins and asphaltenes is 8.8 % and 7.3 %, correspondingly. The yield of solid products and gas is 19.3% and 5.7 %, respectively.

The introduction of water/acetonitrile (bitumen/acetonitrile/water ratio = 4/3/1) results in a significant decrease of the yield of resin in the cracked products from 19.1 % (in cracked products obtained in absence of additives) to 3.9 %, while the proportion of asphaltenes increases from 7.1 % (for cracking in absence of additives) to 25.2 %.

The addition of copper oxide (1 %) to the water/acetonitrile mixture leads to almost two times increase of the yield of gas during the cracking process from 3.4 % (in water/acetonitrile mixture in absence of copper oxide) to 8.5 % (in copper oxide presence). At the same time, the yield of asphaltenes decreases significantly from 25.2 % to 16.9 %.

A mixture of bitumen with isopropanol (77.8 % and 22.2 %, respectively) with the addition of a copper oxide powder (1 mass % of the bitumen content) is fed to a flow reactor. The feed rate is 4 ml/min, while the total mass of the mixture is 200 g. The cracking is carried out at a temperature of 450°C. The heat treatment of the bitumen results in a significant decrease of the content of oils and resins in the composition of the liquid cracking products (Table 5). This is due to the proceeding of compacting reactions of the bitumen components with significant coke formation.

CONCLUSIONS

The conditions of the thermal cracking of natural bitumens of the Beke and Munaily Mola deposits under conditions of a stationary and flow-through installation are worked out. It is shown that by varying the conditions and the additives introduced, it is possible to decrease

significantly the gas and coke formation during the process of bitumen cracking, and to improve essentially the component composition of the resulting liquid products (the “synthetic oil”).

The introduction of additives in the course of the cracking process taking place under stationary conditions leads to an increase of the yield of the gaseous products by 3.4 %- 8.5 %, that of oils by 43.3% - 58.9 % and that of asphaltenes by 7.3 % - 25.2 %). The proportion of the resins is significantly decreased by 3.9 % - 8.8 %).

A high yield of liquid products (75.0 %) and oils (58.9 %) is observed in isopropanol medium in a supercritical environment with the introduction CuO of 1 mass % as a result of the cracking of the Beke deposit bitumen.

REFERENCES

1. A.G. Okunev, E.V. Parkhomchuk, A.I. Lysikov, P.D. Parunin, V.S. Semeikina, V.N. Parmon, Catalytic hydroprocessing of heavy petroleum feedstocks, *Succ. Chem.*, 84, 9, 2015, 987-999, (in Russian).
2. Ye. Tileuberdi, Z.A. Mansurov, Ye.K. Ongarbayev, B.K. Tuleutaev, Structural study and upgrading of Kazakhstan oil sands, *Euras. Chem. Techn. J.*, 17, 2, 2015, 173-179.
3. S. Rudyk, Relationships between SARA fractions of conventional oil, heavy oil, natural bitumen and residues, *Fuel*, 216, 330-340.
4. M. Hosseinpour, S.J. Ahmadi, S Fatemi, Successive co-operation of supercritical water and silica-supported iron oxide nanoparticles in upgrading of heavy petroleum residue: Suppression of coke deposition over catalyst, *J. Sup. Fluids*, 100, 2015, 70-78.
5. F. Eri, S. Shinya, T. Toshimasa, Production of Light Oil by Oxidative Cracking of Oil Sand Bitumen Using Iron Oxide Catalysts in a Steam Atmosphere,

- Ener. Fuels, 25, 2, 2011, 524-527.
6. V.I. Sharypov, N.G. Beregovtsova, S.V. Baryshnikov, B.N. Kuznetsov, Pyrolysis of the oil residue and some organic compounds in a water vapor medium in the presence of hematite, *Chem. for Sustain. Devel.*, 3, 1997, 287-291, (in Russian).
 7. V.I. Sharypov, B.N. Kuznetsov, N.G. Beregovtsova, S.V. Barishnikov, V.N. Sidel'nikov, Steam cracking of coal-derived liquids and some aromatic compounds in the presence of haematite, *Fuel*, 75, 7, 1996, 791-794.
 8. X.Z. Yuan, J.Y. Tong, G.M. Zeng, H. Li, W. Xie, Comparative Studies of Products Obtained at Different Temperatures during Straw Liquefaction by Hot Compressed Water, *Ener. Fuels*, 23, 6, 2009, 3262-3267.
 9. An-gui Zhang, Jinsen Gao, Gang Wang, Chunming Xu, Xinying Lan, Guoqing Ning, Yongmei Liang, Reaction Performance and Chemical Structure Changes of Oil Sand Bitumen during the Fluid Thermal Process, *Ener. Fuels*, 25, 8, 2011, 3615-3623.
 10. Li-Qun Zhao, Zhen-Min Cheng, Yong Ding, Pei-Qing Yuan, Shan-Xiang Lu, Wei-Kang Yuan, Experimental Study on Vacuum Residuuum Upgrading through Pyrolysis in Supercritical Water, *Ener. Fuels*, 20, 5, 2006, 2067-2071.
 11. Zhen-Min Cheng, Yong Ding, Li-Qun Zhao, Pei-Qing Yuan, Wei-Kang Yuan, Effects of Supercritical Water in Vacuum Residue Upgrading, *Ener. Fuels*, 23, 6, 2009, 3178-3183.
 12. V.R. Antipenko, O.A. Golubina, I.V. Goncharov, S.V. Nova, Yu.V. Rokosov, Composition of the products of hydrothermal transformation of natural asphaltit, *Bull. Tomsk Polytech. Univer.*, 308, 6, 2005, 122-127, (in Russian).
 13. V.R. Antipenko, Composition of fraction of oil products of non-isothermal aquatermolise of high-surface natural asphaltit, *Bull. Tomsk Polytech. Univer.*, 319, 3, 2011, 125-129, (in Russian).
 14. N.N. Sviridenko Regularities of thermal transformations of natural bitumens components. PhD thesis - Tomsk, 2016, 134, (in Russian).
 15. Y.K. Ongarbayev, A.K. Golovko, E.B. Krivtsov, Y.I. Imanbayev, E. Tileuberdi, B. Tuleutayev, Z.A. Mansurov, Thermocatalytic cracking of the natural bitumen of Kazakhstan, *Solid Fuel Chem.*, 50, 2, 2016, 81-87.
 16. Y. Imanbayev, Y. Ongarbayev, Y. Tileuberdi, E. Krivtsov, A. Golovko, Z. Mansurov. High temperature transformation of tar-asphaltene components of oil sand bitumen, *Journal of the Serbian Chemical Society*, 82, 9, 2017, 1063-1073.